**Adsorption Kinetics of Organic Compounds on the Bismuth Single Crystal Electrodes**

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Adsorption behaviour of various organic compounds has been studied by electrochemists for a long time as the surface active compounds are involved in the conversion and storage processes of energy and in electrosynthesis, are used as corrosion inhibitors and as catalysts in various electrochemical reactions. In spite of the great interest there are only few works devoted to the problem of the adsorption kinetics of various compounds on single crystal plane electrodes [1,2]. The studies of adsorption kinetics at different single crystal planes are probably able to give some very important additional information on the role of the hydrocarbon chain structure and chemical composition of adsorbate in the formation process of the adsorbed layer and in their molecular structure, *i.e.* in the orientation of molecules adsorbed, in $\pi$-electron system interaction with metal surface, and in the process of the formation of the hydrogen bonds in the inner layer region of electric double layer (edl). This information would be very useful for the simulation of process occurring on the phase boundaries in the living organisms as well as in the other condensed systems.

Cyclic voltammetry and impedance have been employed for the quantitative study of the 2-methyl-2-butanol (*tert*-PenOH), *n*-heptanol (*n*-HepOH), D-ribose and ATP adsorption kinetics on the electrochemically polished (EP) bismuth single crystal plane electrodes from the aqueous 0.05 M $Na_2SO_4$, as well as from 0.05 M $Na_2SO_4$ + 0.01 M $NaH_2PO_4$ + 0.01 M $Na_2HPO_4$ base electrolyte solutions. A non-linear least squares (NLLSF) fitting program [3] has been used for the analysis of experimental complex plane ($Z$",$Z$'-; Nyquist) plots. The results of simulations show that the $Z$",$Z$'-curves for Bi | 0.05 M $Na_2SO_4$ interface can be simulated by the equivalent circuit, which assumes that the interfacial impedance is in the form of a constant phase element with the fractional exponent value very close to unity ($0.97 < \alpha \leq 0.99$). Thus, the EP Bi | 0.05 M $Na_2SO_4$ interface can be taken as an ideally polarizable one.

The complex plane plots for EP Bi | 0.05 M $Na_2SO_4$ + 0.01 M $NaH_2PO_4$ + 0.01 M $Na_2HPO_4$ interface can be simulated by the classical Frumkin–Melik-Gaikazyan circuit [4,5] with the value of double layer capacitance ($C_{dl}$), adsorption capacitance ($C_{ad}$) and Warburg diffusion impedance ($Z_W$) depending on the electrode potential. It was found that in the region of potentials $-0.9 < E < -0.7$ V (SCE), $C_{ad}$ has a maximum indicating that the weak specific adsorption of anions, depending on $E$, is possible. The same effect was established for Hg | 0.5 M $NaCH_3COO$ interface [6]. The NLLSF results show that the deviation of experimental results from simulations increase if the Frumkin–Melik-Gaikazyan–Randels [7], Randels [5], Dolin–Ershler or Damaskin–Grafov (taking into account the conception of the mixed electrolyte) [8] equivalent circuit have been used. According to the data of simulations the adsorption or partial charge transfer resistance $R_{ad}$ has very low values and thus the adsorption of anions on the bismuth single crystal plane electrodes is practically reversible.

The complex plane plots for the interface Bi plane | 0.05 M $Na_2SO_4$ with additions of *tert*-PenOH, *n*-HepOH, D-ribose or ATP indicate that the shape of Nyquist plots noticeably depends on the concentration and chemical nature of compound studied. $Z$",$Z$'-plots for *tert*-PenOH, D-ribose and *n*-HepOH | Bi plane interfaces can be simulated by the classical Frumkin–Melik-Gaikazyan equivalent circuit [2] with $C_{ad}$ and $Z_W$, noticeably depending on the electrode potential as well as on $c_{org}$. The adsorption capacitance has maximum in the region of adsorption-desorption peaks and decreases very quickly to $C_{ad} \sim 0$ in the region of maximal adsorption.

The Warburg diffusion impedance has been simulated by the generalized finite Warburg element (GFW) short circuit terminus model

$$Z_{GFW} = \frac{R_D \tanh\left[(jT\omega)^{\alpha_{org}}\right]}{(jT\omega)^{\alpha_{org}}}$$

where $R_D$ is the so-called limiting diffusion resistance as at very low frequencies $Z$' approaches to $R_D$. The parameter $T$ is expressed as $T = L^2/D$, where $L$ is an effective diffuse layer thickness and $D$ is an effective diffusion coefficient for organic compound. The fractional exponent for the system containing surface active organic compound, $\alpha_{org}$, has values $0.3 \leq \alpha_{org} \leq 1$. According to the results of simulation $R_D$ and $L$ have maximal values in the region of potentials, where $0.5 < \theta < \theta_{max}$ ($\theta$ and $\theta_{max}$ are surface and maximal surface coverages, respectively). The values of $R_D$ decrease and $C_{ad}$ increase in the order of compounds ATP < *n*-HepOH < D-ribose < *tert*-PenOH and in the order of planes Bi($01\bar{1}$) < Bi(111) < Bi(001), *i.e.* with the decrease of adsorption activity and with the rise of Gibbs maximal adsorption. The analysis of complex plane and Cole–Cole plots [2,3] indicates that in the region of moderate *ac* frequencies ($2.0 < f < 2000$ Hz) the adsorption of *tert*-PenOH is mainly limited by the rate of diffusion step, but at $f > 2000$ Hz, the mixed adsorption kinetics (slow heterogeneous adsorption and diffusion steps) is possible. The same is valid for D-ribose and ATP | Bi interface in the range $20 < f < 10000$ Hz. At the moderate $f$ the adsorption of *n*-HepOH is mainly limited by the slow diffusion step. At very low frequencies there is noticeable deviation of systems from the diffusion kinetics and a very slow two-dimensional association process seems to be possible. The effect of two-dimensional association increases in the order *tert*-PenOH < *n*-HepOH < D-ribose.

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